



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP97/04526 <b>(22) International Filing Date:</b> 20 August 1997 (20.08.97) <b>(30) Priority Data:</b> 08/700,979 21 August 1996 (21.08.96) US <b>(71) Applicant (for all designated States except US):</b> NOVARTIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> TERRY, Wilson, Leonard, Jr. [US/US]; 755 Cirrus Drive, Alpharetta, GA 30202 (US). SMITH, Charles, Woolfolk, Jr. [US/US]; 6857 Haskell Drive, Fairview, PA 16415 (US). ATTAWAY, David, Brian [US/US]; 8380-G., Roswell Road, Atlanta, GA 30350 (US). <b>(74) Agent:</b> ROTH, Bernhard, M.; Novartis AG, Patent- und Markenabteilung, Lichtstrasse 35, CH-4002 Basel (CH).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR TREATING MOLDED ARTICLES  <b>(57) Abstract</b>  The invention provides a process for deblocking and extracting a molded article from a mold. The process has the steps of contacting the molded article with an extracting solvent and contacting the molded article with a liquid liquifiable gas, preferably with liquid carbon dioxide. The invention also provides a treating medium for deblocking and extracting a molded article. The medium preferably contains liquid carbon dioxide and an extracting solvent.		

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## METHOD FOR TREATING MOLDED ARTICLES

### Background of the Invention

The present invention relates to cleaning and separating polymeric molded articles. More specifically, this invention relates to deblocking molded articles and removing extractable materials from the article.

A large number of polymeric articles are formed by placing a monomeric or prepolymeric material into a mold and then causing polymerization of the material. Typically, such molded polymeric articles contain impurities and unpolymerized monomeric materials that can be leached out or extracted from the articles. For certain applications, e.g., biomedical devices and ophthalmic lenses, it is important to remove the extractable materials from the polymerized articles since the extractable materials may adversely interact with the biological environment. For example, in conventional processes for manufacturing contact lenses, extractable residual materials from a molded polymeric contact lens are extracted with an organic solvent, such as an alcohol. Although the alcohol extraction process removes undesirable extractable materials, the alcohol remains in the polymeric network of the lens and must be removed before the lens can be further processed or be worn safely. Typically, an alcohol extracted lens is dried to remove the alcohol. However, the drying step is time-consuming and tends to leave dry residue spots on the lens.

An additional problem associated with producing a polymerized article on a mold is that the polymerized article formed on the mold needs to be separated or released from the mold without damaging the molded article and, preferably, without damaging the mold. For example, a critical step in the production of contact lenses using molds is releasing or deblocking the lenses without damaging the lenses from the molds in which the lenses were formed. This separation problem is particularly severe when the molded article contains tacky polymeric material, such as silicone. A conventional method for releasing a contact lens from a mold uses a manual process to gently remove the lens in heated water, for example, disclosed in U.S. Pat. No 5,264,161 to Druskis et al. However, such manual process is labor intensive and prone to defects caused by handling errors. Alternatively, a mold release agent, e.g., a wax or silicone formulation, can be applied on the mold before a polymerizable material is injected into and polymerized in the mold to ensure proper release of the molded article. However, for certain applications, a mold release agent cannot be utilized since the release agent may adversely interact with the polymer of the molded article or the environment in which the molded article is used.

There remains a need for a process that conveniently deblocks a molded article from the mold in which the article was formed and reliably extracts undesirable materials from the molded article. There additionally remains a need for a process that produces substantially dried molded article such that the time-consuming drying step and problems associated with the drying step can be minimized or eliminated.

#### **SUMMARY OF THE INVENTION**

There is provided in accordance with the invention a process for deblocking and extracting a molded article from a mold. The process has the steps of contacting or treating the molded article with a treating solution which contains a liquid liquifiable gas, preferably liquid carbon dioxide. Particularly, the process has the steps of contacting the molded article with an extracting solvent and contacting the molded article with liquid carbon dioxide. The present invention also provides a treating medium for deblocking and extracting a molded article. The treating medium preferably contains between about 50 wt% and about 99 wt% of liquid carbon dioxide and between about 50 wt% and about 1 wt% of an extracting solvent, based on the total weight of the medium.

The process of the invention provides efficient and reliable means for deblocking a molded article from the mold in which the article was formed and extracting undesirable and unpolymerized polymerizable materials from the molded article. The treated molded article produced with the present process is deblocked from the mold and fully extracted as well as substantially or fully dried such that the molded article can be further processed, e.g., coated or plasma treated, or packaged for future use. The present process is particularly suitable for molded articles containing tacky polymeric materials, such as silicone, silicone elastomers and silicone copolymers.

#### **DESCRIPTION OF THE DRAWING**

Fig. 1 illustrates an exemplary treating apparatus suitable for the present deblocking and extracting process.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides a process for deblocking a molded article, especially a molded hydrogel article, from the mold in which the article was formed, and extracting extractable materials from the molded article. The term "hydrogel" as used herein indicates a polymeric material that is capable of absorbing at least about 10 wt% water. The process

provides a deblocked and extracted molded article that is substantially dried, preferably fully dried. The process has the steps of contacting, preferably immersing, a molded article formed in or on a mold with an extracting solvent and contacting, preferably immersing, the molded article with a liquid liquifiable gas, preferably with liquid carbon dioxide. The extracting solvent deblocks the molded article from the mold and extracts extractable materials from the molded article. The preferred liquid carbon dioxide contacting step of the present invention, which is conveniently conducted in a vessel that can be operated under moderately pressurized environment, may sequentially follow the solvent contacting step. Alternatively, the preferred liquid carbon dioxide contacting step can be simultaneously conducted with the solvent contacting step.

In accordance with the present invention, a suitable extracting solvent penetrates the polymeric network of the molded article and causes the polymer of the molded article to swell without causing any significant deterioration or degradation of the polymeric network. Extracting solvents suitable for the present invention include, without limitation thereto, alcohols, preferably alcohols having up to 5 carbon atoms, e.g., ethanol, propanol, isopropanol, butanol, isobutanol and tert-butanol; glycols, preferably glycols having up to 5 carbon atoms, e.g., ethylene glycol and glycerol; ketones, preferably ketones having up to 5 carbon atoms, e.g., acetone; alkanes, preferably alkanes having 5 to 7 carbon atoms, e.g., hexane; aromatic solvents, preferably benzene or benzene substituted by up to three C<sub>1</sub>-C<sub>2</sub> alkyl groups, e.g., toluene and xylene; ethers, preferably ethers having up to 6 carbon atoms; dimethylsulfoxide (DMSO); and dimethylsulfide (DMS). More preferred extracting solvents include alcohols, glycols, ketones, ethers, alkanes and aromatic solvents, including the preferences disclosed hereinbefore. Of the preferred extracting solvents, even more preferred are alcohols and glycols, and most preferred is isopropanol.

The extracting solvent contacting step of the invention may be conducted in ambient environment. Alternatively, the solvent contacting step may be conducted in a pressurizable environment, e.g., in a pressurizable vessel, such that the solvent contacting step and the carbon dioxide contacting step can be conducted in one apparatus. The solvent contacting step can be a single- or multi-step process. Preferably, the solvent contacting step is a step that exposes the molded article to a series of solvent batches such that the polymeric network of the molded article is subjected to a series of solvent exchange substeps. The duration of each solvent exchange substep depends on the type of the polymer that forms the molded article, the type of the extracting solvent used and the size of the molded article. For example, when a siloxane-copolymer hydrogel contact lens on a mold is treated and

isopropanol is used as the extracting solvent, each substep lasts preferably between about 1 minute and about 60 minutes, more preferably between about 2 minutes and about 30 minutes, most preferably between about 5 minutes and about 15 minutes. Alternatively, the extracting solvent contacting step can be conducted in a vessel that continuously feeds and circulates the extracting solvent such that the extracting solvent contacting step is conducted in a continuous fashion. In accordance with the invention, the extracting solvent extracts extractable materials, e.g., unpolymerized monomer or prepolymer and impurities, from the molded article and promotes deblocking of the article from the mold.

Suitable liquid carbon dioxide for the liquid carbon dioxide contacting step of the invention has a pressure at least about 500 psi and a temperature between about 0°C and about 31°C, preferably at the saturation pressure and room temperature. As a preferred embodiment of the present invention, liquid carbon dioxide is used at room temperature, thereby eliminating the need for regulating the temperature of liquid carbon dioxide. Although the present invention is illustrated with liquid carbon dioxide, other liquifiable gases (e.g., nitrous oxide, ethane, propane, ammonia, and azeotropes, e.g., chlorofluorocarbons) can be used. Preferably, a suitable liquifiable gas is in the gaseous phase in ambient environment. The present invention is highly advantageous in that the deblocking and extracting process can be conducted under ambient temperature and moderately elevated pressure and is not as time-consuming and labor-intensive as a conventional organic solvent extraction process. Consequently, the deblocking and extracting process is highly economical when compared to conventional solvent extraction processes and high pressure supercritical fluid extraction processes.

As indicated above, in one embodiment of the invention, the solvent contacting step is followed by the liquid carbon dioxide contacting step. The liquid carbon dioxide replaces the extracting solvent in the polymeric network and further extracts undesirable materials from the polymeric network. The molded article treated with the extracting solvent is placed in a pressurizable vessel and then liquid carbon dioxide is introduced in the vessel, contacting the molded article with the liquid carbon dioxide, preferably immersing the molded article in liquid carbon dioxide. As indicated above, the molded article can be treated in the pressurizable vessel with the extracting solvent so that the solvent treated molded article can be treated with liquid carbon dioxide without the need for additional handling of the molded article. As with the extracting solvent treatment step, the liquid carbon dioxide contacting step may also be conducted in a series of substeps. The duration of each carbon dioxide treating substep depends on the type of the polymer that forms the molded article,

the type of the extracting solvent used and the size of the molded article. For example, when a siloxane-copolymer hydrogel contact lens is treated, each substep may last preferably between about 1 minute and about 60 minutes, more preferably between about 2 minutes and about 30 minutes, most preferably between about 5 minutes and about 15 minutes. After the molded article is treated with liquid carbon dioxide, the liquid carbon dioxide is removed from the vessel and the pressure of the vessel is lowered to ambient pressure. The resulting molded article is deblocked from the mold, extracted and completely or substantially dried.

As another embodiment of the invention, the molded article is simultaneously contacted or treated with a treating mixture that contains the extracting solvent and liquid carbon dioxide. The extracting solvent and liquid carbon dioxide are simultaneously supplied or a mixture of the extracting solvent and liquid carbon dioxide is introduced into the treating vessel which contains the molded articles on molds. Preferably, the treating mixture contains between about 1 wt% and about 50 wt%, more preferably between about 5 wt% and about 40 wt%, most preferably between about 10 wt% and about 30 wt%, of an extracting solvent and between about 99 wt% and about 50 wt%, more preferably between about 95 wt% and about 60 wt%, most preferably between about 90 wt% and about 70 wt%, of liquid carbon dioxide, based on the total weight of the treating mixture. The simultaneous treating step may also be conducted in a series of substeps, and the duration of the treating step or substeps depends on the type of the polymer that forms the molded article, the type of the extracting solvent and the size of the molded article. For example, when a siloxane-copolymer hydrogel contact lens is treated, each substep may last preferably between about 1 minute and about 60 minutes, more preferably between about 2 minutes and about 30 minutes, most preferably between about 5 minutes and about 15 minutes. The present simultaneous treating process simultaneously deblocks the molded articles from the molds and extracts extractable materials from the molded articles. The molded articles treated with the simultaneous treating process are substantially dried. However, the deblocked and extracted molded article can be further dried in a conventional manner, e.g., vacuum dried, before the article is further processed. As a preferred embodiment of the invention, the molded articles that are subjected to the simultaneous treatment process are again treated with liquid carbon dioxide so that the extracted and deblocked molded articles are fully dried and the extracting solvent is fully removed from the molded articles.

Hydrogel molded articles which may be treated in accordance with the present invention include a wide variety of polymeric articles which are formed by initiating polymerization of a

monomeric or pre-polymeric mixture in a mold. Examples of such polymeric articles include, without limitation thereto, medical devices and components, such as drug delivery devices (transdermal, ophthalmic, parenteral, etc.) and components thereof; and, in particular, ophthalmic devices including vision correction devices, such as contact lenses, ocular implants, ocular onlays, and components thereof.

Hereinafter, the present invention is illustrated with ophthalmic lenses for illustration purposes. Ophthalmic lenses, e.g., contact lenses and intraocular lenses, that can be treated with the present process contain various hydrogel-forming monomers, including hydroxyesters of acrylic or methacrylic acid, e.g., hydroxyethyl methacrylate (HEMA), hydroxyoctyl methacrylate, hydroxyethyl acrylate, glyceryl methacrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, methacrylic acid (MAA), hydroxyethyl methacrylamide (HMA), dimethylacrylamide (DMA), N-vinylpyrrolidone (NVP); polyorganosiloxanes, e.g. disclosed in U.S. Pat. Nos. 3,996,187 and 3,341,490; polyoxyalkylene, e.g., disclosed in European Patent Application 614 921; glucose-oxyethyl methacrylate; methacryloyl glucose; and copolymers of cyclic polyol and polyalkylether. Further suitable ophthalmic lenses are siloxane-copolymer hydrogel ophthalmic lenses, for example, as disclosed in WO 96/31792, which application in its entirety is herein incorporated by reference.

Turning to the figure, Fig. 1 illustrates an exemplary apparatus suitable for the present invention. More particularly, Fig. 1 illustrates a lens-treating apparatus 10, which can be sealed and operated under pressurized environment. The apparatus 10 is surrounded with insulation 12 sufficient to maintain the applied fluid at the desired temperature and pressure ranges. Trays 14 support a plurality of lenses 16 affixed to molds 18. The support trays either have perforations or are sufficiently porous to allow the treating fluids to flow through the trays. The trays 14 with the lenses 16 on the molds 18 are loaded into lens-treating apparatus 10, either manually or via an automated lens distribution system. The treating fluids, either sequentially or simultaneously as discussed above, enter through inlet 20 to fill the apparatus 10. At a point near the top of apparatus 10, the treating fluids pass through a flow distribution member 24, which distributes the fluids uniformly across a cross-section of the apparatus perpendicular to the flow. The treating fluids flow through the trays 14, contacting the lenses 16 and the molds 18. Although the treating process can be conducted without any extraneous agitation means, the apparatus 10 may optionally be equipped with agitation means 22 to provide uniform distribution of the treatment fluids in the apparatus.



Although the above apparatus is illustrated as a batch apparatus, the invention is not limited thereto. The treating fluids can be supplied into the apparatus in a continuous fashion. In addition, the contact lenses 16 on the molds 18 can be passed through the lens-treating apparatus 10 in a continuous manner known in the production engineering art. For example, the treatment fluids flow through the trays 14 and the contact lenses 16 and the molds 18 before exiting through a fluid outlet, which is not shown. Preferably, the speed of the treatment fluids contacting the lenses 16 is such that the fluids contact the lenses 16 in a turbulent fashion.

The present invention is further illustrated with the following examples. However, the examples are not to be construed as limiting the invention thereto. Temperatures are given in degrees Celsius.

**Example 1:** Siloxane-copolymer hydrogel contact lenses are produced in a double-sided molding process. A polysiloxane macromer is prepared. 51.5 g (50 mmol) of the perfluoropolyether Fomblin® ZDOL (from Ausimont S.p.A, Milan) having a mean molecular weight of 1030 g/mol and containing 1.96 meq/g of hydroxyl groups according to end-group titration is introduced into a three-neck flask together with 50 mg of dibutyltin dilaurate. The flask contents are evacuated to about 20 mbar with stirring and subsequently decompressed with argon. This operation is repeated twice. 22.2 g (0.1 mol) of freshly distilled isophorone diisocyanate kept under argon are subsequently added in a counterstream of argon. The temperature in the flask is kept below 30°C by cooling with a waterbath. After stirring overnight at room temperature, the reaction is complete.

202 g of the  $\alpha,\omega$ -hydroxypropyl-terminated polydimethylsiloxane KF-6001 from Shin-Etsu having a mean molecular weight of 2000 g/mol (1.00 meq/g of hydroxyl groups according to titration) are introduced into a flask. The flask contents are evacuated to approx. 0.1 mbar and decompressed with argon. This operation is repeated twice. The degassed siloxane is dissolved in 202 ml of freshly distilled toluene kept under argon, and 100 mg of dibutyltin dilaurate (DBTDL) are added. After complete homogenization of the solution, all the perfluoropolyether reacted with isophorone diisocyanate (IPDI) is added under argon. After stirring overnight at room temperature, the reaction is complete. The solvent is stripped off under a high vacuum at room temperature. Microtitration shows 0.36 meq/g of hydroxyl groups (theory 0.37 meq/g). 13.78 g (88.9 mmol) of 2-isocyanatoethyl methacrylate (IEM) are added under argon to 247 g of the  $\alpha,\omega$ -hydroxypropyl-terminated polysiloxane-perfluoropolyether-polysiloxane three-block copolymer (a three-block copolymer on

stoichiometric average, but other block lengths are also present). The mixture is stirred at room temperature for three days, and the macromer produced is dried.

13.0 g of the macromer are dissolved in 5.6 g of ethanol (Fluka, puriss. p.a.) (70% by weight solution). After complete homogenization of the solution, 5.2 g of 3-tris(trimethyl-siloxy)silylpropyl methacrylate (TRIS from Shin-Etsu, product No. KF-2801), 7.8 g of freshly distilled dimethylacrylamide and 160 mg of photoinitiator Darocur® 1173 (Ciba) are added. This solution is filtered through a Teflon membrane having a pore width of 0.45 mm under an argon pressure of from 1 to 2 atm. The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert-gas atmosphere, where the solution is pipetted into dust-free contact-lens (polypropylene) molds having concave and convex mold halves. The molds are closed, and the polymerization reaction is effected by UV irradiation (15 mW/cm<sup>2</sup>, 5 min.), with simultaneous crosslinking.

The concave mold halves are manually removed, leaving the lenses predominately affixed to the convex mold halves. 60 lenses affixed convex mold halves are placed inside the treatment cavity of an Autoclave Engineering model EP-2000 Supercritical CO<sub>2</sub> Treatment System, which is equipped with a magnetic stirrer. 7 liter of 100% isopropanol is fed to the cavity and the magnetic stirrer was set at 800 rpm. After 1 hour of the isopropanol treatment, isopropanol is drained from the cavity, and the cavity is sealed. While maintaining the treatment system at 25°C, carbon dioxide is fed into the cavity until the pressure reached 1400 psi, providing liquid carbon dioxide environment. After several minutes, carbon dioxide was evacuated from the cavity. The liquid carbon dioxide treatment is repeated two more times, and the lenses are taken out.

The resulting lenses are deblocked from the molds and are fully dried without dry spots. The lenses are clear and undamaged, demonstrating the efficacy of the present invention.

**Example 2:** The procedure outlined in Example 1 is repeated, except the untreated lenses on the molds are manually deblocked. The deblocked lenses are dried under vacuum over night, and the weight of the lenses are measured. The dried lenses are carefully placed over the molds, thereby reattaching the lenses on the molds. The lenses on the molds are

again subjected to the above-described isopropanol and liquid carbon dioxide treatments. The resulting lenses are again measured for their weight.

The difference between the initial weight and the final weight of the lenses indicates the amount of extractable materials removed from the lenses, and the amount of extracted material is about 6 wt% of the initial lens weight, which is slightly higher than the amount of extractable materials that is extracted with a conventional isopropanol extraction process that immerses the lens in 100% isopropanol for about 24 hours and then vacuum dries the extracted lens.

**Example 3:** The procedure outlined in Example 1 is repeated, except isopropanol and carbon dioxide are fed simultaneously into the treatment system to obtain 30 wt% isopropanol and 70 wt% liquid carbon dioxide treating mixture at 25°C and 1400 psi. After one hour of the mixture treatment, the treating mixture is evacuated from the cavity and the mixture treatment is repeated. After the second treatment, the lenses are taken out of the treatment cavity.

The above examples clearly demonstrate that the present molded article treating process efficiently and economically deblocks the molded articles from the molds and extracts undesirable materials from the molded articles without causing damages to the molded articles and without the problems associated with conventional labor-intensive and time-consuming extraction processes.

What is claimed is:

1. A process for deblocking and extracting a molded article from a mold, which process comprises the steps of contacting said molded article with an extracting solvent and contacting said molded article with a liquid liquifiable gas.
2. The process of claim 1 wherein said extracting solvent is selected from the group consisting of alcohols, glycols, ketones, ethers, alkanes and aromatic solvents.
3. The process of claim 1 wherein said liquifiable gas is liquid carbon dioxide.
4. The process of claim 2 wherein said extracting solvent is isopropanol.
5. The process of claim 1 wherein said molded article is an ophthalmic device.
6. The process of claim 5 wherein said molded article is a contact lens.
7. The process of claim 1 wherein the solvent contacting step and the liquid liquifiable gas contacting step are sequentially conducted.
8. The process of claim 7 wherein the liquid liquifiable gas is liquid carbon dioxide.
9. The process of claim 1 wherein the solvent contacting step and the liquid liquifiable gas contacting step are conducted simultaneously by providing a mixture of said extracting solvent and said liquid liquifiable gas.
10. The process of claim 9 wherein the liquid liquifiable gas is liquid carbon dioxide.
11. The process of claim 10 wherein said mixture comprises between about 1 wt% and about 50 wt% of said extracting solvent and between about 99 wt% and about 50 wt% of liquid carbon dioxide.
12. The process of claim 3 wherein said liquid carbon dioxide is supplied at a temperature between about 0°C and about 31°C and at a pressure at least about 500 psi.

13. A process for deblocking and extracting a molded article from a mold, which process comprises contacting said molded article on said mold with a treating solution, said treating solution comprising a liquid liquifiable gas.

14. A process according to claim 13 wherein the liquid liquifiable gas is liquid carbon dioxide.

15. The process of claim 13 wherein said treating solution further comprises an extracting solvent selected from the group consisting of alcohols, glycols, ketones, ethers, alkanes and aromatic solvents.

16. The process of claim 15 wherein said treating solution comprises between about 1 wt% and about 50 wt% of said extracting solvent and between about 99 wt% and about 50 wt% of liquid carbon dioxide.

17. The process of any of claims 13 or 14 wherein said treating solution has a temperature between about 0°C and about 31°C.

18. The process of claim 17 wherein said treating solution comprises about 1 wt% and about 50 wt% of isopropanol and between about 99 wt% and about 50 wt% of liquid carbon dioxide.

19. A treating medium for deblocking and extracting a molded article, comprising between about 1 wt% and about 50 wt% of an extracting solvent and between about 99 wt% and about 50 wt% of liquid carbon dioxide.

20. The treating medium of claim 19 wherein said extraction solvent is selected from the group consisting of alcohols, glycols, ketones, ethers, alkanes and aromatic solvents.

21. The treating medium of claim 20 wherein said treating medium has a temperature between about 0°C and about 31°C.

22. A hydrogel article treated with the treating medium of claim 18.

23. A hydrogel molded article produced in accordance with the process of claim 3.

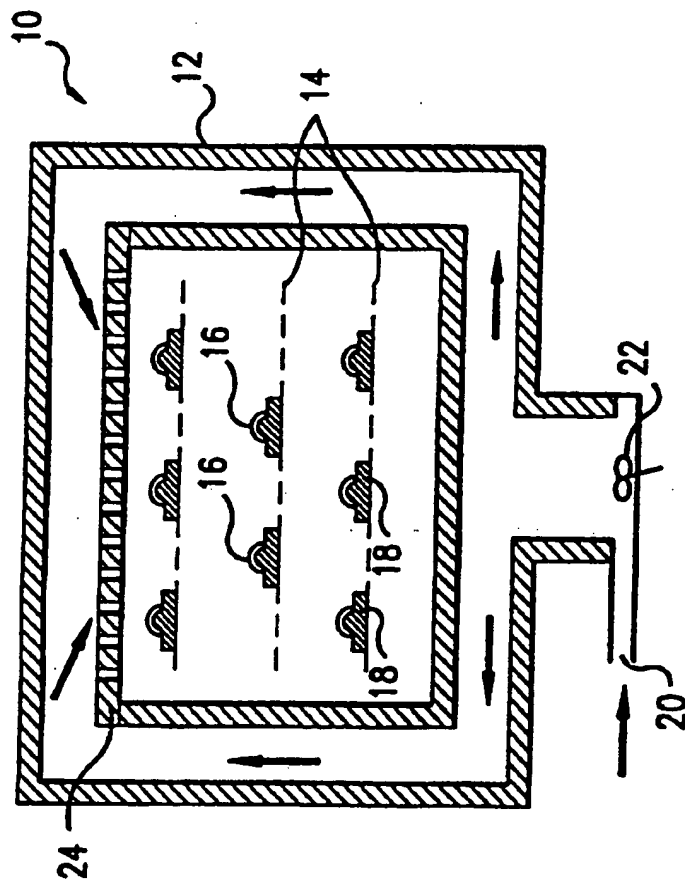


FIG.1

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/04526

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B29C33/60 B29D11/00 //B29L11:00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29C B29D G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 20476 A (BAUSCH & LOMB INCORPORATED) 3 August 1995 see the whole document see page 8, line 23 - page 9, line 8 ---	1-23
X	EP 0 370 268 A (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) 30 May 1990 see the whole document see table 1 see page 11, line 24 - line 56 see page 12, line 48 - line 51 see claims 1,5,9,10 --- -/--	1-4,7-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN  vol. 96, no. 2, 29 February 1996  &amp; JP 07 266443 A (HOYA CORP.), 17 October 1995,  see abstract  &amp; DATABASE WPI  Section Ch, Week 9550  Derwent Publications Ltd., London, GB;  Class ADP, AN 95-389491 (50)  &amp; JP 07 266 443 A (HOYA CORP.) , 17  October 1995  see abstract</p> <p>-----</p>	1,3,5,6



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/04526

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EP 370268 A	30-05-90	US 4882107 A AT 126752 T AU 631381 B AU 4379489 A CA 2001704 A,C DE 68923931 D DE 68923931 T ES 2075841 T JP 1960789 C JP 2212107 A JP 6088255 B KR 9507143 B	21-11-89 15-09-95 26-11-92 31-05-90 23-05-90 28-09-95 04-01-96 16-10-95 10-08-95 23-08-90 09-11-94 30-06-95